

# Pore structure of TiO<sub>2</sub>-modified ZrO<sub>2</sub> particles prepared by the glycothermal method

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**Abstract:** Titania-modified zirconia was synthesized via thermal reaction of zirconium *n*-propoxide and titanium isopropoxide in 1,4-butanediol at 300 °C. The obtained powders were spherical particles composed of TiO<sub>2</sub>-ZrO<sub>2</sub> solid solution nanocrystals. The product had a large surface area (160 m<sup>2</sup>/g) and a relatively narrow pore size distribution. After calcination at high temperatures, the TiO<sub>2</sub>-modified ZrO<sub>2</sub> sample preserved large surface areas and narrow pore size distributions, and these results indicate superior thermal stability of this material.

**Keywords:** ZrO<sub>2</sub>, Glycothermal method, Pore structure.

## 1. Introduction

Zirconia and zirconia-based oxides have been used as catalysts and catalysts supports for various reactions, and improvement in the thermal stability and control of the morphology as well as pore structure of these materials are of great importance. Recently, synthesis of spherical metal oxide particles with homogeneous size and shapes have been correcting much attention to improve catalyst performance. A sol-gel method is one of the preferable methods for this purpose [1, 2]; however, the obtained products are amorphous or oxides with low crystallinity, and heat treatment are necessary to obtain well-crystallized products. On the contrary, it is previously reported that spherical zirconia particles composed of nanocrystalline zirconia were directly obtained via thermal reaction of zirconium alkoxide in 1,4-butanediol (glycothermal method) [3]. Furthermore, it is also reported that an addition of small amounts of TiO<sub>2</sub> significantly improved the thermal stability of the zirconia-based oxides materials [4]. In this study, titania-modified zirconia samples were prepared by the glycothermal method and their morphology, thermal stability and pore structure were investigated.

## 2. Experimental

Zirconium *n*-propoxide (19.77 g) and titanium isopropoxide (2.32 g, Ti/Zr = 0.136) were suspended in 1,4-butanediol (100 mL) and the mixture was placed in a 300-mL autoclave. After the atmosphere of inside the autoclave was replaced with nitrogen, the mixture was heated to 300 °C at a rate of 2.5 °C min<sup>-1</sup>, and kept at that temperature for 2 h under the autogenous pressure of the solvent. After the glycothermal reaction for 2 h, the valve of the autoclave was slightly opened to remove organic vapor from the autoclave by flashing evaporation while keeping the temperature at 300 °C. After cooling, dry powders were obtained directly. The products were calcined at a prescribed temperature for 1 h in a box furnace.

Powder X-ray diffraction patterns were collected on a Rigaku RINT 2200VF using CuK $\alpha$  radiation. Scanning electron microscopy measurement was performed on a JEOL JSM-6510AS. Specific surface area was calculated using the BET multipoint method with a Quantachrome Instruments NOVA 2200e. Pore size distribution was calculated on the basis of N<sub>2</sub> adsorption isotherm using the BJH method.

## 3. Results and discussion

In Figure 1, SEM images of the ZrO<sub>2</sub> and TiO<sub>2</sub>-modified ZrO<sub>2</sub> obtained by the glycothermal method are shown. The ZrO<sub>2</sub> powders were spherical particles with ~10  $\mu$ m size. For TiO<sub>2</sub>-modified ZrO<sub>2</sub>, spherical particles with smaller size were observed. After calcination at 600 °C, the particle sizes of these samples became slightly smaller; however, spherical shapes were preserved. In Figure 2, XRD patterns of the

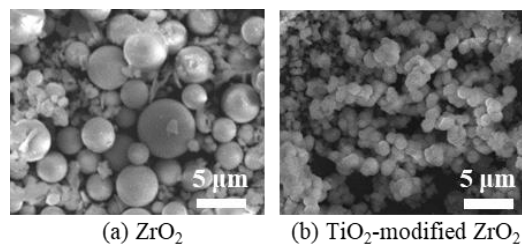
products are depicted. For the as-synthesized ZrO<sub>2</sub>, a tetragonal phase was mainly observed and as the calcination temperature increases the tetragonal phase transformed to a monoclinic phase. As shown in Table 1, the ZrO<sub>2</sub> sample had a quite large surface area; however, the surface area decreased significantly after calcination at higher temperature. On the contrary, the XRD patterns of the TiO<sub>2</sub>-modified ZrO<sub>2</sub> did not change significantly, and higher surface areas are preserved even after calcination at 600 °C. In Figure 3, N<sub>2</sub> adsorption isotherms and pore size distributions of the ZrO<sub>2</sub> and TiO<sub>2</sub>-modified ZrO<sub>2</sub> are shown. The shape of isotherm was classified as type IV with hysteresis loop, and corresponding mesopore peaks can be seen in the pore size distributions. For the ZrO<sub>2</sub> samples, the pore volume decreased gradually as the increase in the calcination temperature. A shift in the pore size distribution to larger side was also recognized. On the contrary, the pore volumes for TiO<sub>2</sub>-modified ZrO<sub>2</sub> samples, which were much larger than those of the ZrO<sub>2</sub> samples, did not decrease after the calcination at 600 °C. In addition, the pore size distributions for TiO<sub>2</sub>-modified ZrO<sub>2</sub> was narrower than those of ZrO<sub>2</sub> samples. These results indicate superior properties of this sample for catalytic applications.

#### 4. Conclusions

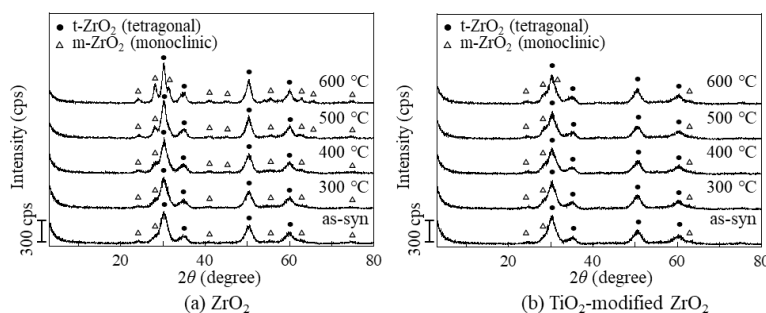
By thermal reaction of zirconium *n*- and titanium alkoxides in 1,4-butanediol at 300 °C, spherical particles composed of nanocrystalline TiO<sub>2</sub>-modified ZrO<sub>2</sub> were obtained. The thus obtained TiO<sub>2</sub>-modified ZrO<sub>2</sub> had large surface area, pore volume, and narrow pore size distribution. Even after calcination at 600 °C, the sample preserved large surface area and pore structure.

#### References

1. C. Zhang, C. Li, J. Yang, Z. Cheng, Z. Hou, Y. Fan, J. Lin, *Langmuir*, 25 (2009) 7078.
2. H. Uchiyama, K. Takagi, H. Kozuka, *Colloids and Surfaces A*, 403 (2012) 121.
3. S. Kongwudthiti, P. Praserttham, P. Silveston, M. Inoue, *Ceram. Intern.*, 29 (2003) 807.
4. K. Kubo, S. Hosokawa, S. Furukawa, S. Iwamoto, M. Inoue, *J. Mater. Sci.*, 43 (2008) 2198.



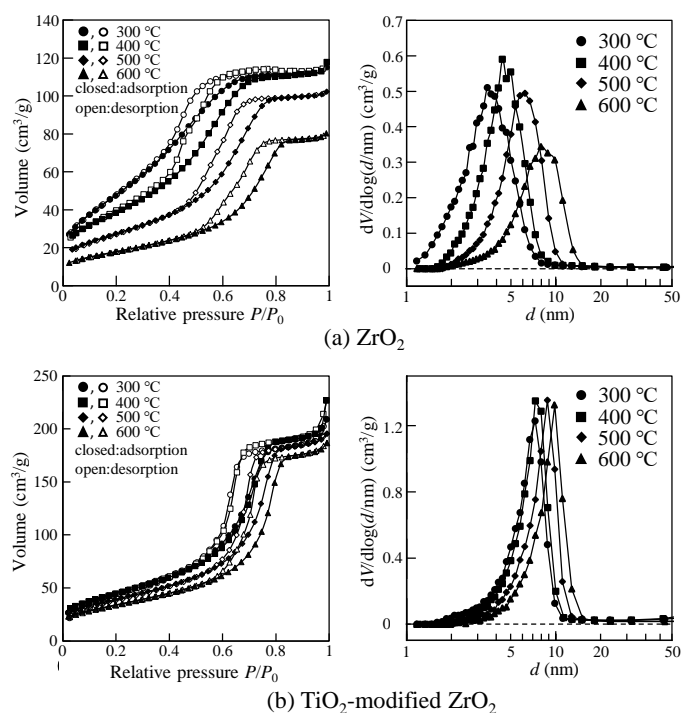
**Figure 1.** SEM images of (a) ZrO<sub>2</sub> and (b) TiO<sub>2</sub>-modified ZrO<sub>2</sub> prepared by the glycothermal method.



**Figure 2.** XRD patterns of (a) ZrO<sub>2</sub> and (b) TiO<sub>2</sub>-modified ZrO<sub>2</sub>.

**Table 1.** Physical properties of ZrO<sub>2</sub> and TiO<sub>2</sub>-modified ZrO<sub>2</sub>

Calcination temperature (°C)	BET surface area (m <sup>2</sup> /g)		Pore volume (cm <sup>3</sup> /g)	
	ZrO <sub>2</sub>	TiO <sub>2</sub> -ZrO <sub>2</sub>	ZrO <sub>2</sub>	TiO <sub>2</sub> -ZrO <sub>2</sub>
300	192	167	0.18	0.32
400	124	162	0.18	0.35
500	111	141	0.16	0.30
600	57.9	122	0.12	0.29



**Figure 3.** N<sub>2</sub> adsorption isotherm and pore size distribution of (a) ZrO<sub>2</sub> and (b) TiO<sub>2</sub>-modified ZrO<sub>2</sub>.